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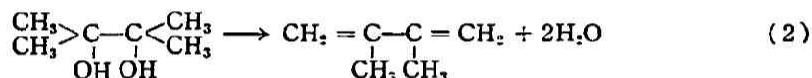
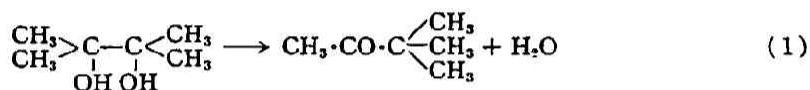
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DEHYDRATION OF PINACOL UNDER PRESSURE

By SHIGERU MINOMURA

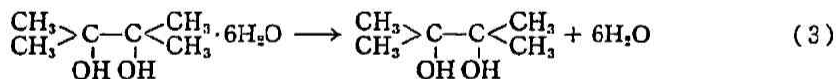
Introduction

It is well known that pinacol is changed into pinacol in by the dehydration of one water molecule and into 2, 3-dimethylbutadiene-(1, 3) by the dehydration of two water molecules according to the following chemical equations on boiling with dilute acids, such as sulphuric¹⁾, phosphoric, oxalic, or tartaric acid²⁾, or with $\text{H}_2\text{SO}_4 \cdot 3\text{H}_2\text{O}$ ³⁾, and on contacting with conc sulphuric acid at 0° C⁴⁾, or with aluminium oxide at about 350° C⁵⁾. The reaction (1) is pinacolonic rearrangement.



The mechanism has been studied by a number of investigators⁶⁻⁸⁾ and explained by the theory of pinacolonic electron displacement at present. The reaction (2) is a manufacturing method of 2,3-dimethylbutadiene-(1, 3) which is a monomer of methyl rubber.

Pinacol anhydrate combines with water and pinacol hydrate containing six molecules of crystallization water is obtained from an aqueous solution⁹⁻¹¹⁾. The hydrate decomposes easily into anhydrate and water by distillation¹¹⁾ and also by drying over conc sulphuric acid below atmospheric pressure (10 ~ 30 mmHg)^{12, 13)} as follows.



The author examined the possibility of the dehydration reactions (1) ~ (3) above de-

- 1) R. Fittig, *Ann. Chem.*, 110, 23 (1859)
- 2) D. Vorländer, *Ber.*, 30, 2266 (1897)
- 3) T. Kuwata, *J. Chem. Soc. Japan*, 62, 1028 (1941)
- 4) R. Scholl and C. Born, *Ber.*, 28, 1364 (1895)
- 5) W. Ipatjeff, *Chem. Zentralbl.* (1901) II, 87
- 6) E. Erlenmeyer, *Ber.*, 14, 322 (1881)
- 7) M. Tiffnean, *Compt. rend.*, 143, 684 (1906)
- 8) R. Roger and W. B. McKay, *J. Chem. Soc.*, 332 (1933)
- 9) R. Fittig, *Ann. Chem.*, 110, 27 (1859), 114, 55 (1860)
- 10) G. Städeler, *ibid.*, 111, 278 (1859)
- 11) Beilstein, *Organische Chemie*, Vierte Auflage, Band I, p. 487, Pinakon
- 12) T. Amemiya, *J. Chem. Soc. Japan*, 63, 1214 (1942)
- 13) K. A. Krasuskü and S. Mamedov, *Chem. Abst.* 5378 (1938)

scribed by compressing pinacol hydrate, or anhydrate, or mixtures of pinacol and various added materials, such as KCl, silica gel, α -alumina, γ -alumina, or filter paper, which were effective in the urea synthesis by the dehydration of solid ammonium bicarbonate¹⁴⁾, up to 17,280 atm at 26°~29°C, and discussed the pressure effect on pinacol hydrate and anhydrate crystals from the results obtained.

Experimentals

(I) Materials

(1) **Pinacol hydrate** Pinacol hydrate was prepared by reducing acetone with magnesium turnings and mercuric chloride according to the procedure of R. Adams¹⁵⁾. It was purified by recrystallizing from an aqueous solution. The melting point was found to be 45.6° C, though it had been published as 45°~46° C in literature^{3, 11, 12, 13)}.

(2) **Pinacol anhydrate** Pinacol anhydrate was prepared by extracting water completely from a benzene solution of pinacol hydrate by means of a Soxhlet's extractor and by fractionally distilling the solution. The boiling point was found to be 174.4°C and the melting point 45.0° C, though the boiling and melting points cited in literature^{8, 16)} were 173°~175° C and 45° C respectively.

(3) **Added materials** (a) Silica gel: Commercial silica gel was heated at about 300°C for 8 hours. (b) Alumina: Aluminium nitrate was heated at about 450°C and washed with water. α -Alumina was prepared by again heating at about 1000° C for 15 hours. γ -Alumina was prepared by heating at about 450° C for 12 hours after washing. (c) KCl and filter paper: Commercial materials for analysis were used after drying.

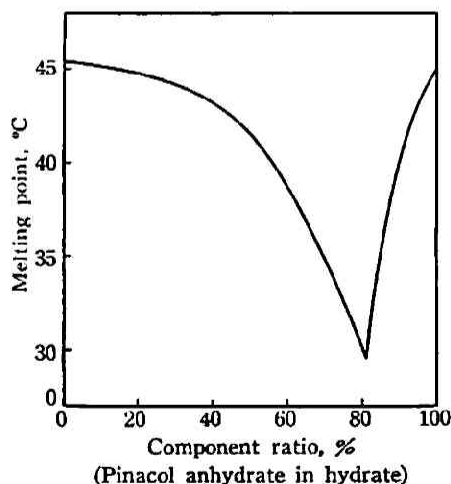


Fig. 1

(II) Determination of products

(1) **Pinacol anhydrate in hydrate** The contents of pinacol anhydrate in hydrate were determined by the melting point. The elevation rate of temperature during the measurement was fixed in all cases. The melting point of pinacol hydrate was found to be 45.6° C and that of anhydrate 45.0° C. The melting points of mixtures of the two forms of pinacol decrease¹⁶⁾. The relation between the melting points and component ratios of pinacol hydrate and anhydrate is obtained in Fig. 1. The melting points decrease from 45.6° C with the increase of the contents of anhydrate in hydrate.

14) R. Kiyama and T. Yanagimoto, *This Journal*, **21**, 32 (1951)

15) R. Adams, *Organic Syntheses*, Collect. Vol. I, 87 (1925)

16) H. A. Iddles, A. W. Low, B. D. Rosen, and R. T. Hart, *Ind. Eng. Chem., Analyt. Ed.*, **11**, 102 (1939)

The maximum depression of the melting point to 29.5°C is observed by a mixture with 81.1 % anhydrate. The melting point increase again with lower degree of hydration and is found to be 45.0°C in anhydrate.

(2) **Pinacolin** The following procedure was carried out according to the method of Iddles, Low, Rosen, and Hart¹⁶⁾. A given amount of the sample was dissolved in extra pure ethyl alcohol not containing ketone and aldehyde. A 2N-hydrochloric acid solution of 2, 4-dinitrophenylhydrazine was poured into the sample solution and it was left for over 24 hours. Pinacolin was settled down as 2, 4-dinitrophenylhydrazone. The precipitate was filtered by a glass filter, and washed with 2N-hydrochloric acid and water, and dried in an air-bath at 105°C, and weighed.

(3) **2, 3-Dimethylbutadiene-(1, 3)** A few drops of tetranitromethane were poured into an ethyl alcohol solution of the sample according to the procedure of Werner¹⁷⁾ and Ostromisslensky¹⁸⁾. When the sample contains a double bond compound, the colour of the solution becomes yellow. This colour reaction is effective to a trace of double bond compound which can not be detected by the other method. Tetranitromethane was prepared from mixing absolute nitric acid (density 1.53) with acetic acid anhydride¹⁹⁾. Another quantitative analysis was tried by adding bromine to the double bond, using pyridine bromide sulphate²⁰⁾.

(III) **Procedure** Pinacol hydrate, or anhydrate, or mixtures of equal amount of pinacol and added material (KCl, silica gel, α -alumina, or γ -alumina), or several thin layers pillup alternately pinacol and filter paper were compressed for a definite time up to 17,280 atm at 26° ~ 29°C. The contents of pinacol anhydrate in hydrate compressed with filter paper, and that of pinacolin, or of 2, 3-dimethylbutadiene-(1, 3) in pinacol hydrate or anhydrate compressed with various added materials were determined by the above described methods.

The high pressure apparatus was the same as the previous reports^{21, 22)}.

Experimental results

(I) **Depression of melting point** Pinacol hydrate prepared began to melt at 45.5°C and completely at 45.6°C. The melting point was determined clearly. The melting point of pinacol hydrate compressed with filter paper for 10 minutes up to 8,640 atm was found not to change. But under 11,800 ~ 17,280 atm the sample began to melt at 40.2°C and completely at 45.4°C. The content of pinacol anhydrate in hydrate corresponding to the melting point is within a few per cent according to Fig. 1. The depression of

17) A. Werner, *Ber.*, 42, 4324 (1909)

18) I. Ostromisslensky, *ibid.*, 43, 197 (1910)

19) F. D. Chattaway, *J. Chem. Soc.*, 97, 2099 (1910)

20) K. W. Rosenmund, *Z. angew. Chem.*, 37, 58 (1924)

21) R. Kiyama, *This Journal*, 19, 1 (1945)

22) R. Kiyama and T. Yanagimoto, *ibid.*, 21, 32 (1951)

melting point was not found in the case of compressing pinacol hydrate only. The extension of compression time (1/2 or 3 hours) was not also effective both in the compression of pinacol hydrate only and with filter paper.

(II) **Formation of pinacolin** The yield of pinacolin dehydrated by compressing pinacol hydrate, or anhydrate, or mixtures of pinacol and various additional materials under 7,560, 15,120, and 17,280 atm at 26°~29°C for 1/2 hours is shown in Table 1. Pinacolin was not produced in the case of compressing pinacol only, but produced in the amount of 10⁻² % order in compressing with an added material. It increased with pressure, although the tendency was not remarkably observed.

Table 1
The yield (in 10⁻² %) of pinacolin dehydrated
from pinacol under pressure

Atm Add. material	Pinacolin from pinacol hydrate					Pinacolin from pinacol anhydrate			
	none	KCl	silica gel	α - alumina	γ - alumina	none	KCl	α - alumina	filter paper
7,560	0	5	4	3	4	0	—	—	—
15,120	0	7	7	3	5	0	8	7	3
17,280	0	8	7	4	7	0	—	—	—

(III) **Formation of 2, 3-dimethylbutadiene-(1, 3)** It was found from the colour reaction that a double bond compound was produced by compressing pinacol hydrate with KCl or silica gel under 7,560, 15,120, and 17,280 atm at 26°~29°C for 1/2 hour. The formation of double bond was not found by adding bromine, using pyridine bromide sulphate, as the amount of double bond was a trace. The colour of the sample compressed at 17,280 atm was deeper yellow than that at 7,560 atm. No colour reaction was observed in compressing pinacol hydrate only. The determination of double bond by the colour reaction with tetranitromethane was not suitable for the compression of a mixture of pinacol hydrate and α or γ -alumina.*

Discussions

The chemical reaction of a solid material by compression is chiefly owing to the decrease of a molecular volume, or the shearing at the boundary of particles. The molecular volumes of pinacol anhydrate²³⁾, 2, 3-dimethylbutadiene-(1, 3)²⁴⁾, water²⁵⁾ at 15°C, and pinacolin²⁶⁾ at 16°C calculated from their densities under atmospheric pressure

* An alcohol solution of pinacol hydrate with α or γ -alumina was coloured by tetranitromethane, whether compressed or not.

23) C. D. Hodgman, "Handbook of Chemistry and Physics", p. 762 (1939)

24) Courtot, *Bull. soc. chim.*, [3], 35, 979

25) *International Critical Tables*, Vol. III, p. 25 (1928)

26) R. Fittig, *Ann. Chem.*, 114, 58 (1860)

are 122.179, 112.407, 18.032, and 125.211 cc/mole respectively. The molecular volumes in the final state in the reactions in which one or two molecules of water were dehydrated from pinacol anhydrate increase more by 21.064 or 26.292 cc/mole than those in the initial state respectively. The molecular volume of pinacol hydrate like many other hydrates with six water molecules is smaller than the total volumes of pinacol anhydrate and six molecules of water, though the numerical values are unknown. Postulating the difference of molecular volumes between the final and initial states is scarcely change by compression, it may be considered that the dehydration of pinacol hydrate or anhydrate as the obtained results is not attributed to the change of molecular volume, but to the shearing between the particles. Besides, it is found that the shearing is more effective by compressing with hard materials, considering the result that the dehydration of a mixture of pinacol and an added material was easier than that of pinacol only.

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